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12) **PATENT APPLICATION** **A1**

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56) **List of documents cited in the preliminary search report:**
See the end of the present document packet.

60) **References to other related French documents:** [blank]

71) **Applicant(s):** COMMISSARIAT À L'ENERGIE ATOMIQUE [Atomic Energy Commission], a Scientific, Technical, and Industrial Establishment, domiciled in France.

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74) **Agent:** Brevatome.

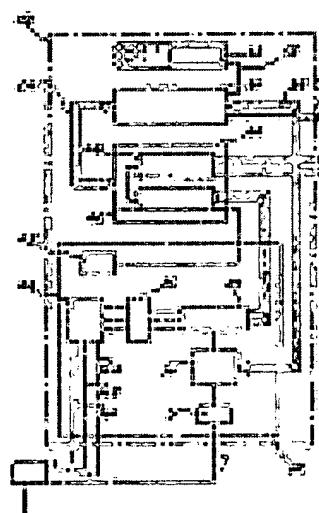
54) **Autonomous device for reading an active chemical sensor having at least one optical fiber, and procedure for its implementation.**

57) Modulated excitation means [34] excite an active chemical sensor [1] over a plurality of wavelengths; synchronous detection means [40] analyze the light power conveyed by the sensor [1]; processing means [50] calculate, based on the demodulated signals, the absorbance of the sensor [1] and then determine the pH of the medium in which the sensor [1] is immersed, through the application of a relationship [R₁]:

$$\text{pH} = \text{pK} - \log \left(\frac{\text{Amax} - \text{A}}{\text{A} - \text{Amin}} \right)$$

where pK, Amax, and Amin are previously determined parameters, and A is the absorbance of the sensor [1].

Application to the measurement of pH and pCO₂ values.



**AUTONOMOUS DEVICE FOR READING AN ACTIVE
CHEMICAL SENSOR HAVING AT LEAST ONE OPTICAL FIBER,
AND PROCEDURE FOR ITS IMPLEMENTATION.**

Descriptive memorandum

The present invention relates to an autonomous device for reading an active chemical sensor having at least one optical fiber, and a procedure for its implementation. It is applicable specifically to the measurement of the pH value and of the pCO₂ (partial carbon dioxide pressure) of a solution.

Active chemical sensors with optical fibers, also known as "optodes" or "optrodes," allow pH measurements to be made over broad ranges and at distances, if necessary, of up to several hundred meters.

For more information about optodes and their operation, reference may be made to the publication by G. Boisdé and J.J. Perez, entitled "Optodes: A new generation of sensors," in *La vie des sciences [Life of the Sciences]*, Reports, General Series, Volume 5, No. 5 (1988), pp. 303–332.

The device according to the invention relates to sensors for which a pH value is determined based on an absorbance measurement. A description of such sensors is found, for example, in document No. FR-A-2 613 074, filed in the name of the present applicant, or in the article by G. Boisdé et al. entitled "Comparisons between two dye-immobilization techniques on optodes for the *[sic]* pH measurement by absorption and reflectance," which appeared in *SPIE*, Vol. 1172 (Chemical, Biochemical, and Environmental Sensors) (1989), pp. 239–250.

The article by K.T.V. Grattan, Z. Mouaziz, and R.K. Selli, which appeared in *Proc. SPIE (Int. Soc. Opt. Eng.)*, [Vol.] 798 (1987), pp. 230–237, describes a first type of reading device for the determination of a pH value based on absorbance measurements. This device allows the excitation of the sensor at two different wavelengths. The light sources that are utilized, which consist of light-emitting diodes (LEDs), are modulated in such a way that the sensor is excited in an alternating manner. The detection is performed by a single photodetector, which is placed in operation during time windows corresponding to an excitation at one or the other of the wavelengths.

The article by M. Bacci, F. Baldini, F. Cosi, G. Conforti, and A.M. Schleggi, which appeared in *Proc. SPIE (Int. Soc. Opt. Eng.)*, [Vol.] 1014 (1988), pp. 73–76, describes another type of device that uses the modulation of two LEDs, so as to enable easy demodulation on the first and second harmonics of the signal supplied by a single photodetector.

Other known devices use as many photodetectors as there are excitation wavelengths, with each photodetector being equipped with an appropriate filter.

Most of the known reading devices are not autonomous. They rely on separate processing units, of the microcomputer type. Therefore, they cannot easily be taken out of the laboratory in order to be used on industrial sites.

Furthermore, these devices usually allow only one pH measurement to be made over a limited range, such as, for example, for measurements of blood pH over the range of 7.2 \pm 0.2 pH units, in which case the pH is deduced from the measurement of the absorbance of the sensor by means of a linear law that limits the scope of use of the device.

The device that is the subject of the present invention remedies these disadvantages. It is completely autonomous, which allows easy transport and utilization options. Moreover, the pH is deduced from the absorption by means of a non-linear law (in accordance with a sigmoid function), which expands its scope of applicability.

More specifically, the invention relates to a device for reading an active chemical sensor having at least one optical fiber, which sensor allows absorbance measurements to be made. The reading device includes:

- Excitation means for the sensor delivering at least two beams of light at different wavelengths;
- Modulation means delivering modulation signals at outputs connected to the excitation means;
- Means for detecting a light signal, delivering an electrical detection signal at an output;
- Synchronous demodulation means connected to the output of the detection means and to the outputs of the modulation means, and delivering, at the outputs, as many demodulated signals as there are excitation wavelengths;
- Processing means connected to the outputs of the synchronous demodulation means, which processing means are suitable for determining at least one pH value based on the measurement of the absorbance of the sensor at the various different wavelengths.

The modulation signals are preferably square waves and have different modulation frequencies, which modulation frequencies [F/2] [F/4] are harmonic pairs of a fundamental modulation frequency [F].

The square-wave signals have only odd harmonics, which facilitates the demodulation on the even harmonic signals.

The excitation means advantageously deliver a beam of light at a wavelength located in an absorption valley of the chemical sensor that is utilized.

The excitation means advantageously include electroluminescent diodes, each of which is connected to several optical fibers, which optical fibers are arranged, in alternation, in a ring-shaped pattern.

The optical fibers connected to the various different electroluminescent diodes enable the transport of the optical excitation signals over long distances, which can be as long as several hundreds of meters.

The arrangement in a ring-shaped pattern allows good distribution of the excitation light at the input to the sensor, and therefore greater efficiency of the absorbance measurement.

In one specific embodiment of the invention, the detection means include an optical fiber connected to a photodetector and a programmable amplifier connected to an output of the said photodetector and to the processing means to control the gain of the said amplifier.

The reading device advantageously includes temperature-measurement means connected to the processing means, in order to correct any thermal drifts.

This way, the temperature drifts of the electroluminescent diodes can be automatically compensated, through the application of corrective coefficients determined during prior measurements.

The present invention also relates to a procedure for the implementation of such a measurement device. According to this procedure, for the determination of a pH value, a relationship of the following type is applied:

$$\text{pH} = \text{pK} - \log \left(\frac{\text{Amax} - \text{A}}{\text{A} - \text{Amin}} \right)$$

where pK, Amax, and Amin are previously determined parameters, and A is the absorbance of the sensor as deduced from the detected light signal.

It should be recalled that the absorbance A of an optode is defined by $A = \log P_0/P$, where P_0 is the optical power conveyed by the optode immersed in a reference medium and P is the optical power conveyed by the optode immersed in the medium whose pH is to be determined.

The use of a non-linear relationship for the determination of the pH makes it possible to expand the range of use of the device. In point of fact, the devices in the prior art allow only one single interpretation of the absorbance measurement in the linear portion of the relationship.

The values of pK, Amax, and Amin (which represent, respectively, the pH value at the point of inflection of the sigmoid curve and the limit absorbances of the sensor in question) are advantageously determined during the measurements obtained beforehand with three solutions whose pH value is known.

One of these prior measurements preferably defines a reference for determining the absorbance of the sensor being utilized.

The values of pK, Amax, and Amin are preferably determined on the basis of two simultaneous measurements at two different wavelengths, one of which wavelengths is located in an absorption valley of the chemical sensor that is utilized.

The wavelength located in an absorption valley serves as an internal reference, which makes it possible to avoid the effects of any fluctuations that are not directly related to the pH value.

Thus, in the relationship that yields the pH as a function of the absorbance, A represents the difference $(\text{Am} - \text{Av})$ between the values Am and Av, which correspond respectively to the wavelengths λ_m and λ_v , which latter wavelength is located in an absorption valley of the sensor.

The characteristics and advantages of the invention will be better understood through a reading of the following description, which is offered for explanatory purposes and which is in no way limitative. This description refers to the attached drawings, on which:

- Figure 1 is a schematic representation of a piece of pH measurement equipment that includes a measurement device according to the invention;
- Figure 2 is a schematic representation of a photometric unit contained within the measurement device according to the invention;
- Figure 3 is a schematic representation of a set of optical fibers for connecting an optode to a measurement device;
- Figure 4 is a schematic representation of the square-wave modulation signals utilized in the invention;
- Figure 5 is a schematic representation of an absorbance curve for an optode as a function of the excitation wavelength; and
- Figure 6 is a schematic representation of the calibration points on the sigmoid curve for the interpretation of the absorbance measurements.

Figure 1 is a schematic representation of a piece of pH measurement equipment, in which an optode [1] is connected, by means of a set of optical fibers [Fe1] [Fe2] [Fe3] [Fd] to a reading device [30] according to the invention.

The latter device includes a photometric unit [32], a conversion unit [44], a control and processing unit [50], and a keyboard/display unit [52]. The units [44] and [50] are interconnected by a system bus [54]. The units [32] and [52] are connected to the control unit by means of their parallel port [56] and through one of their two serial ports [57], respectively, with the other serial port [58] being reserved for a connection with a printer (not shown).

Figure 2 shows a example of an implementation of the photometric unit [32]. The latter unit includes excitation means [34] consisting of three light-emitting diodes [DEL1] [DEL2] [DEL3], emitting beams of light at three different wavelengths λ_1 λ_2 λ_3 , respectively. [DEL1] may be a diode that is sold by the Stanley company under reference No. HAY 5566X and that emits a [beam of] light centered on wavelength $\lambda_1 = 590$ nm; [DEL2] may be a diode that is sold by the Stanley company under reference No. HAY 5566X and that emits a [beam of] light centered on wavelength $\lambda_2 = 620$ nm; and [DEL3] may be a diode that is sold by the Philips France company under reference No. CQF 24 and that emits a [beam of] light centered on wavelength $\lambda_3 = 830$ nm.

The light-emitting diodes [DEL1] [DEL2] [DEL3] are connected to the optode [1] by three sets of optical fibers [Fe1] [Fe2] [Fe3], respectively.

As can be seen in Figure 3, each set of optical fibers includes three optical fibers. The optical fibers associated with the diodes [DEL1] [DEL2] [DEL3] are grouped and arranged, in alternation, in a ring-shaped pattern. This arrangement allows good distribution of the excitation light in the optode [1]. The optical fibers [Fe1] [Fe2] [Fe3] are (for example) made of silicon, with a core having a diameter of 200 microns.

The optical fibers [Fe1] [Fe2] [Fe3] are distributed around the optical fiber [Fd] that connects the optode [1] to a photodetector [D]. The optical fiber [Fd] is (for example) made of silicon, with a core having a diameter of 400 microns.

Returning now to Figure 2, we see that the light-emitting diodes [DEL1] [DEL2] [DEL3] are connected to modulation means [36]. The said means [36] include an oscillator [360] that delivers a square-wave signal modulated at a frequency [2F] (for example, 6 KHz). This signal is applied at the input of a divider [362] that delivers a first modulation signal at a frequency [F]. This first modulation signal is divided by 2 by a divider [364] that delivers a second modulation signal at a frequency [F/2]. The second modulation signal is likewise divided by 2, by a divider [366], which delivers a third modulation signal at a frequency [F/4].

Figure 4 is a schematic representation of the square-wave modulation signals at the frequencies [F] [F/2] [F/4]. It is known that square-wave signals have only odd harmonics (F/3, F/5, etc.). Therefore, the use of even harmonic modulation signals for a modulation frequency at a frequency [F] facilitates the synchronous detection. In point of fact, the modulation-frequency harmonics and the modulation frequencies themselves have very different values.

Returning again to Figure 2, we see that the modulation signals at the frequencies [F] [F/2] [F/4] are delivered to the input of an interface circuit [368] that is connected to the light-emitting diodes [DEL1] [DEL2] [DEL3]. This interface circuit [368] controls the modulation of the diodes, ensuring good stability of the modulation signals and eliminating the risks of intermodulation while the diodes are being controlled. For example, the diode [DEL1] is modulated at the frequency [F] (for example, 3 KHz); the diode [DEL2] is modulated at the frequency [F/2], and the diode [DEL3] is modulated at the frequency [F/4].

Thus, the light-emitting diodes [DEL1] [DEL2] [DEL3] emit beams of light that are modulated, respectively, at the frequencies [F] [F/2] [F/4]. Part of these beams of light is absorbed by the optode [1], and part is reflected and transmitted by the optical fiber [Fd] to the photodetector [D], which may consist, for example, of a silicon photodiode of the type sold by the Hamamatsu company under reference No. 1336-5BK.

The detector [D] delivers an electrical signal that is proportional to the luminous intensity that is detected. This signal is amplified by a programmable amplifier [38]. The gain of this amplifier is controlled by the control and processing unit [50], to which it is connected by means of a specific bus [56]. The amplifier [38] includes a preamplifier [380], which may, for example, be programmable by decades, with a first transimpedance stage. The preamplifier [380] is connected to a voltage amplifier [382], which may, for example, be programmable by half-decades.

The amplifier [38] delivers a signal to an input of the demodulation means [40]. The said demodulation means [40] include as many pathways as there are excitation light beams modulated at different frequencies. In the example shown in Figure 3, the demodulation means [40] have three pathways. Each pathway has a bandpass [401] [402] [403] that filters, respectively, at one of the frequencies [F] [F/2] [F/4] (i.e., for the first, second, and third pathways, respectively). For each pathway, the bandpass filter is connected to a synchronous detector [411] [412] [413]. These synchronous detections are, for example, of the type described in French patent No. 86-07809, filed in the name of the present applicant.

The synchronous detection means [40] include a bandpass filter [401] connected to two amplifiers whose outputs are complementary in phase (+1 and -1). An electronic switch consisting of analog gates (for example, of the type sold by the Siliconix brand [*sic*] under reference No. DG[]) selects, in alternation, one or the other of these outputs, at the cadence of the synchronization signal. If the synchronization signal is in phase with the measurement signal, the device performs a detection function in double alternation.

The value of this technique is that when it is used in combination with a bandpass filter [421] located at the output, it enables efficient measurement of alternating signals buried in the noise. In point of fact, when a modulation frequency on the order of several KHz is selected, the 1/f noise (which is significant below 100 Hz) can be avoided. The noise passband is centered on the modulation frequency, and its width is determined by the cut-off frequency of the associated

bandpass filter [421]. The choice of this cut-off frequency is based on a compromise between the response time and the residual noise.

The use of this technique, in combination with an amplification channel with switchable gains, enables very broad measurement dynamics.

The sole function of the bandpass filters [401] located at the input of the synchronous detection means is to pre-condition the signal, by preventing the synchronous detection circuits from departing from their linear functional domain due to the effect of noise and frequency fluctuations, which domain is very different from that of the modulation signal.

The synchronous detection means [411] for the first pathway are controlled by the modulation signal at a frequency [F]; the synchronous detection means [412] for the second pathway are controlled by the modulation signal at a frequency [F/2]; and the synchronous detection means [413] for the third pathway are controlled by the modulation signal at a frequency [F/4].

Each pathway also includes, connected to the synchronous detection means, a low-pass filter [421] [422] [423] that determines the analog response time of the pathways. This response time is, for example, equal to a few tenths of a second.

Each low-pass filter [421] [422] [423] delivers an output signal that corresponds to the response of the sensor [1] to excitation by one of the beams of light.

Returning yet again to Figure 2, we see that the photometric unit [32] includes temperature-measurement means [42], for example, of the type designated as "AD 590 F," which deliver a temperature signal to an output.

In Figure 1, we see that the signals delivered by the demodulation means and the temperature signal are applied to the inputs of the analog-to-digital converter [46], which converts these analog signals to digital signals that can then be processed. These signals make it possible to deduce the absorbance of the optode and to determine the pH of the medium in which the optode is immersed.

These digital signals are processed by the control and processing unit [50], which may be a processor sold by the Gespac company under reference No. SBS 6. The processor [50] communicates with the rest of the device via the bus [54], which, for example, may be of the type sold by the Gespac company under reference No. G 96.

The control and processing unit [50] is connected by means of a serial link [57] to a keyboard/display unit [52], of the microterminal type sold by the Burr Brown company under reference No. TM 2500. This microterminal [52] serves as a control panel. Keys on the keyboard make it possible to select the operating mode of the device (e.g., measurement of the reference light levels, measurement of optical densities or absorbance, calibration of the optode being utilized, or measurement of the pH).

To determine the absorbance, the digital signals corresponding to the response by the optode at the various different wavelengths represent the light power P conveyed by the optode, and the absorbance is obtained by applying relationship [R₀]:

$$A = \log (P_0/P)$$

where P_0 is the optical power conveyed by the optode immersed in a reference medium. Thus, optode absorbances are obtained for each excitation wavelength. To determine the pH, the following relationship, designated as [R₁] in the remainder of this description, is applied:

$$pH = pK - \log \left(\frac{A_{max} - A}{A - A_{min}} \right)$$

This relationship is a sigmoid (i.e., S-shaped) function.

With reference now to Figure 5, which represents the absorbance of an optode as a function of the excitation wavelength, we can discern the meanings of A_{max} , A_{min} , and A .

The measurement of the absorbance of the optode is performed at the wavelength λ_m , which may be equal to λ_1 or λ_2 , depending on the dye utilized in the optode. For example, the wavelength λ_1 , which is equal to 590 nm, is appropriate for TBPSP (tetrabromophenol-sulfonephthalein) dye, [i.e., Bromophenol Blue], and the wavelength λ_2 , which is equal to 620 nm, is appropriate for bromothymol blue.

The wavelength λ_v corresponds to an absorption valley of the optode. In the example of the embodiment described, the wavelength λ_3 is equal to λ_v . As we shall see, it serves as an internal reference.

For a given wavelength located essentially on an absorption peak, the absorption depends on the pH of the medium in which the optode is immersed. In Figure 5, the three curves C₁, C₂,

and C3 correspond respectively to increasingly acidic mediums (or increasingly less basic mediums, or to a transition from a basic medium to an acidic medium).

The variable Amax (curve C1) is defined as the difference between the maximum absorbance at the measurement wavelength and the absorbance at the wavelength λv .

The variable Amin (curve C3) is defined as the difference between the minimum absorbance at the measurement wavelength and the absorbance at the wavelength λv .

The variable A (curve C2) is equal to the difference between the absorbance at the measurement wavelength of the sensor in the medium into which the sensor is immersed and the absorbance at the wavelength λv .

By selecting these definitions, we avoid any baseline fluctuations that are not directly related to the pH value.

The determination of the pH of the medium in which the optode is immersed, based on a measurement of the absorbance and the application of the relationship [R₁], requires the determination beforehand of the parameters pK, Amax, and Amin.

This prior determination is made during the calibration of the optode being utilized. The said calibration consists of immersing the optode successively in three buffer solutions whose pH is known. The first solution, designated as "Standard R," is also taken as a reference for the absorbance measurements (because it defines the power [P₀] used in the absorption calculation, which requires assuming that the absorbance of the optode is null when the optode is immersed in solution R). The other two solutions are designated as "Standard E" and "Standard F," respectively.

The determination of the pK, Amin, and Amax parameters is based on the solution of the system of three equations with three unknowns, as obtained by applying the relationship [R₁] to each of the standards. Thus, we obtain:

$$pK = \log \frac{(A_F - A_E)10^{(pH_E + pH_F)} + A_E10^{(pH_R + pH_E)} - A_F10^{(pH_R + pH_F)}}{(A_F - A_E)10^{pH_R} + A_E10^{pH_F} - A_F10^{pH_E}}$$

$$Amin = -A_E \frac{10^{(pH_E - pK)} + 1}{10^{(pH_E - pH_R)} - 1}$$

$$A_{\text{max}} = -A_{\text{min}} \cdot 10^{(pK - pH_R)}$$

The variables pH_R , pH_E , and pH_F are, respectively, the pH values of the R, E, and F standards. A_E and A_F correspond to the absorbances measured for the E and F standards, and A_R is set as null, by definition. These different parameters are given with reference to Figure 6, representing the calibration points on the sigmoid curve.

Once these parameters have been determined, the pH of a tested sample is calculated by the control and processing unit [50], through the application of the relationship [R₁], after measurement of the absorbance of the optode being utilized.

The reliability of the absorbance measurements, and thus of the determination of the pH value, depends on the stability of the emissions of light by the light-emitting diodes [DEL1] [DEL2] [DEL3] (see Figure 2). Now, we know that these diodes are very sensitive to the temperature changes that inevitably occur in a housing that contains electronic devices. The changes in temperature cause changes in the emission wavelengths, which perturb the absorbance measurements. To mitigate this disadvantage, the temperature of the photometric unit [32] is measured continuously, by means of the temperature sensor [42] (see Figure 1). The analog temperature signal delivered by this sensor [42] is converted to a digital temperature signal by the conversion unit [44]. The digital temperature signal is read by the control and processing unit [50]. Depending on the temperature, a correction factor is applied to the absorbance as measured. The correction factors, which correspond primarily to the [temperature] drifts of each of the light-emitting diodes, are determined experimentally during preliminary tests.

As explained above, the reading device performs the complete processing of the sigmoid [curve] corresponding to the relationship [R₁], which has the effect of expanding the pH range that can be used with a given optode.

However, a reading device according to the invention also enables simplified processing, which has the advantage of allowing the sensor to be calibrated with only two buffer solutions (Standard R and Standard E). Thus, the pH is determined through the application of a relationship [R₂]:

$$pH = aA + b, \text{ where } b = pH_R$$

$$a = \frac{pH_E - pH_R}{A_E}$$

with the same notations as above (see Figure 6).

The optode reading device according to the invention is a high-performance tool. Its broad measurement range, which is obtained thanks to synchronous-detection signal processing, makes it suitable for a variety of optodes. Its photometric precision, supported by good thermal stability, allows it to reach a level of precision that is limited only by that of the associated optode.

Last, the reading device according to the invention is a compact and portable device, which is extremely well suited to field measurements in geochemistry, blood pH measurements, and other types of measurements.

Naturally, the invention is in no way limited to the embodiments that have been described specifically and illustrated herein. In particular, the implementation procedure, including the application of the relationship [R₁], should be understood as being applicable to an optode that uses multiple dyes. In point of fact, the simultaneous use of a plurality of excitation beams at different wavelengths makes it possible to decouple the absorption measurements associated with the various different dyes.

Furthermore, the number of light-emitting diodes is not limited to three. Apart from the light-emitting diode that emits a beam [of light] at a wavelength that corresponds to an absorption valley for the dyes, it is possible, without departing from the scope of the invention, to use more than two light-emitting diodes that are modulated at different frequencies and at the even harmonics of a fundamental modulation frequency.

Other parameters, such as the partial CO₂ pressure (for example, for a blood environment), can be deduced automatically, based on the determination of the pH value.

Claims

1. Device for reading an active chemical sensor having at least one optical fiber, characterized in that the said device includes:
 - Excitation means [34] for the sensor [1] delivering at least two beams of light at different wavelengths;
 - Modulation means [36] delivering modulation signals at outputs connected to the excitation means [34];
 - Means [38] [D] [Fd] for detecting a light signal, delivering an electrical detection signal at an output;
 - Synchronous demodulation means [40] connected to the output of the detection means [38] [D] [Fd] and to the outputs of the modulation means [36], and delivering, at the outputs, as many demodulated signals as there are excitation wavelengths;
 - Processing means [50] connected to the outputs of the synchronous demodulation means [40], which processing means [50] are suitable for determining at least one pH value based on the measurement of the absorbance of the sensor [1] at the various different wavelengths.
2. Device according to Claim 1, characterized in that the said modulation signals are square waves and have different modulation frequencies, which modulation frequencies [F/2] [F/4] are harmonic pairs of a fundamental modulation frequency [F].
3. Device according to Claim 1, characterized in that the said excitation means [34] deliver a beam of light at a wavelength located in an absorption valley of the chemical sensor [1] that is utilized.
4. Device according to Claim 1, characterized in that the said excitation means [34] include light-emitting diodes [DEL1] [DEL2] [DEL3], each of which is connected to several optical fibers, which optical fibers are arranged, in alternation, in a ring-shaped pattern.

5. Device according to Claim 1, characterized in that the said detection means include an optical fiber [Fd] connected to a photodetector [D] and a programmable amplifier [38] connected to an output of the said photodetector [D] and to the processing means [56] to control the gain of the said amplifier [38].
6. Device according to Claim 1, characterized in that it includes temperature-measurement means [42] connected to the processing means [50], in order to correct any thermal drifts.
7. Procedure for the implementation of a device according to Claim 1, characterized in that, for the determination of a pH value, a relationship $[R_1]$ of the following type is applied:

$$pH = pK - \log \left(\frac{A_{max} - A}{A - A_{min}} \right)$$

where pK , A_{max} , and A_{min} are previously determined parameters, and A is the absorbance of the sensor as deduced from the detected light signal.

8. Procedure according to Claim 7, characterized in that pK , A_{max} , and A_{min} are determined during prior sensor calibration measurements performed with three solutions [R] [E] [F] whose pH is known.
9. Procedure according to Claim 8, characterized in that one of the said prior measurements defines a reference for determining the absorbance of the sensor [1] that is utilized.
10. Procedure according to Claim 7, characterized in that A_{max} , A_{min} , and A are determined based on two simultaneous measurements taken at two different wavelengths, one of which wavelengths is located in an absorption valley of the chemical sensor [1] that is utilized.

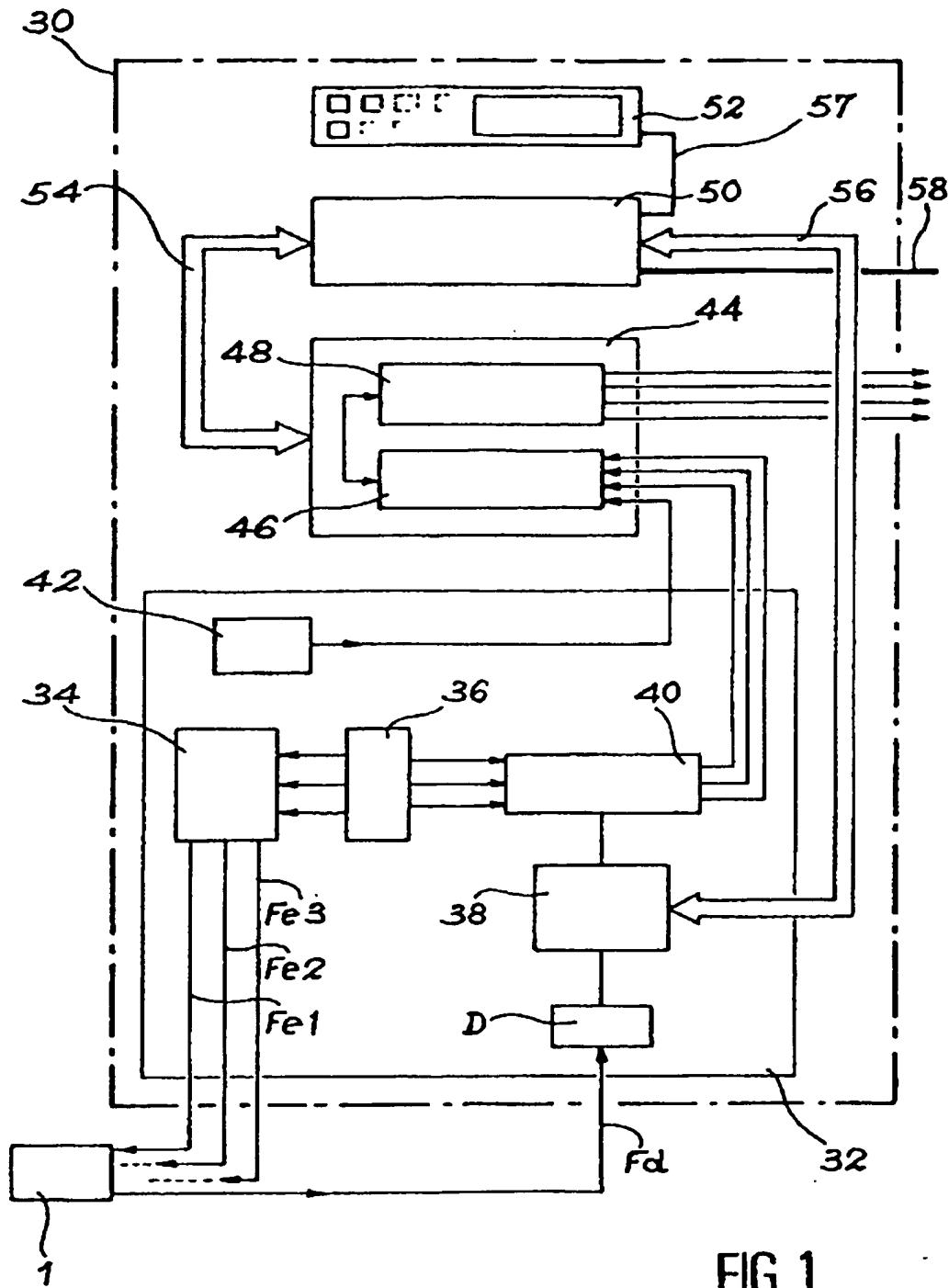


FIG. 1

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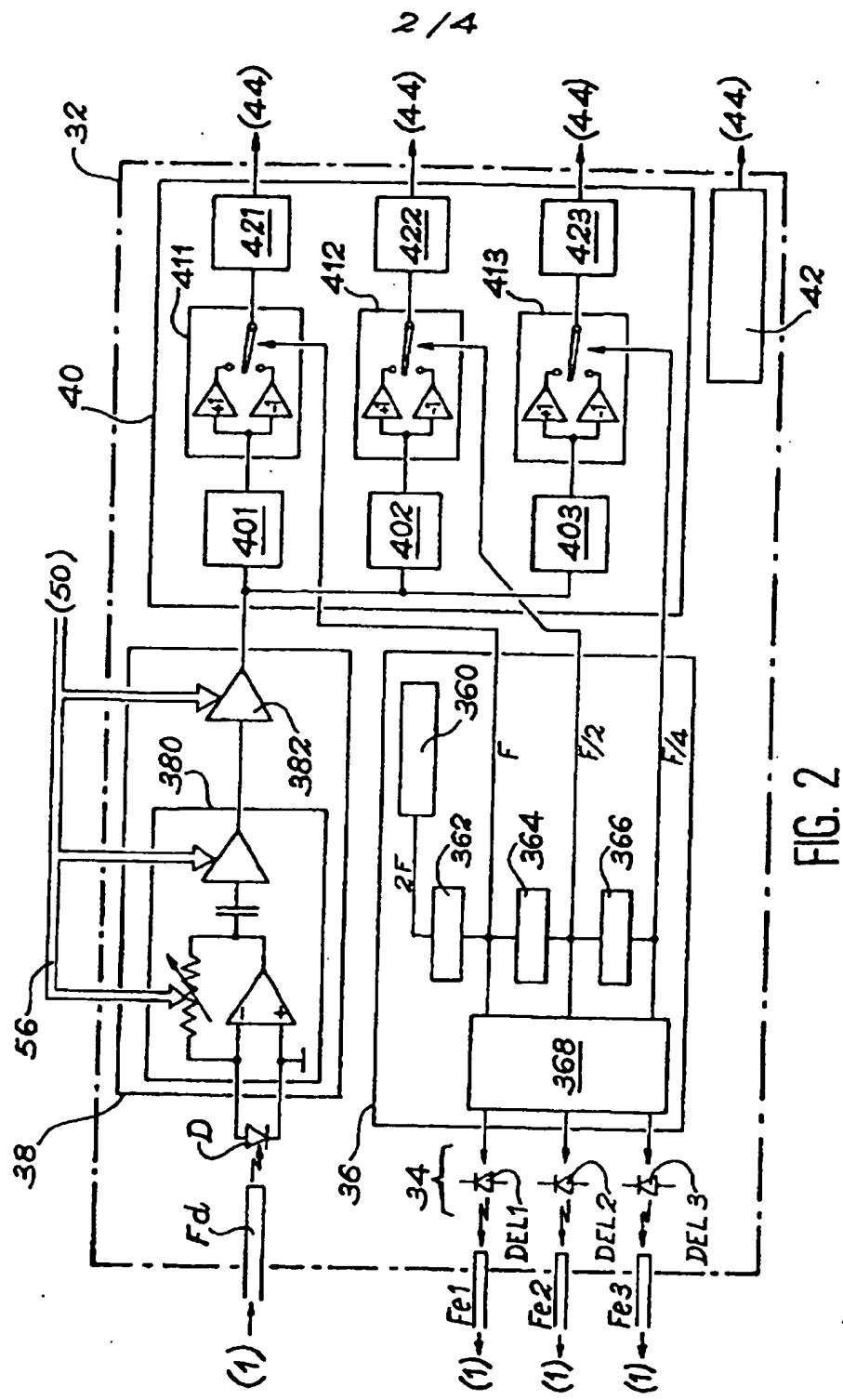


FIG. 2

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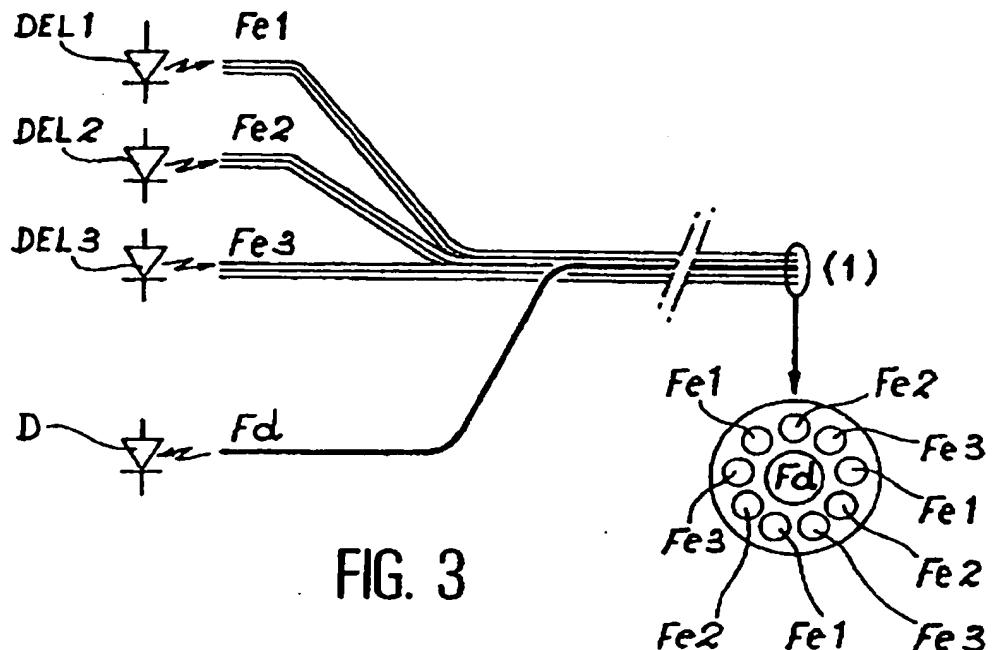


FIG. 3

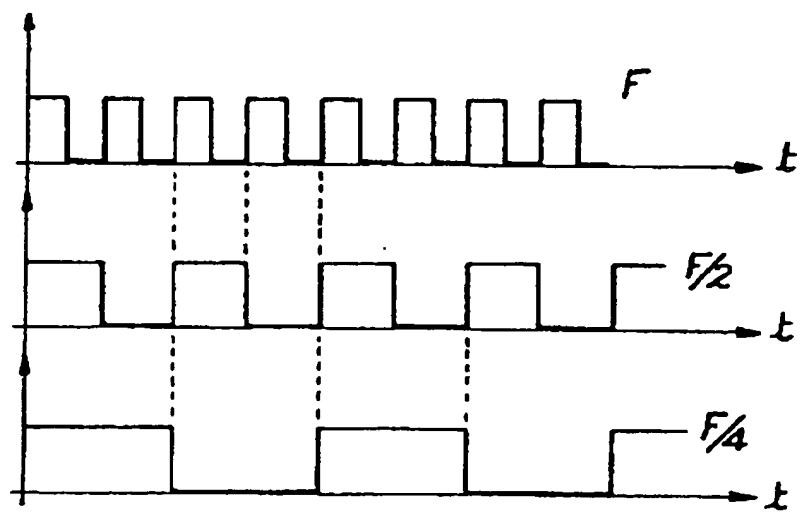


FIG. 4

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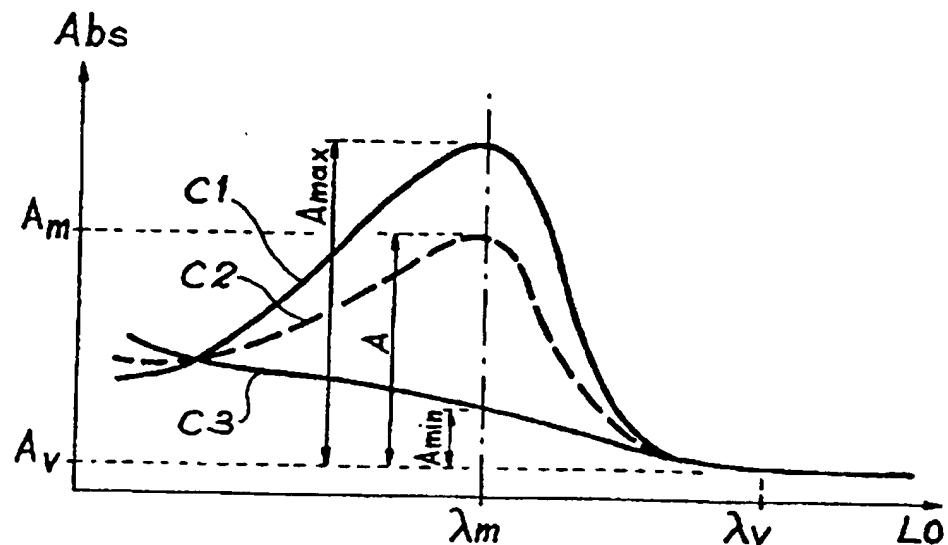


FIG. 5

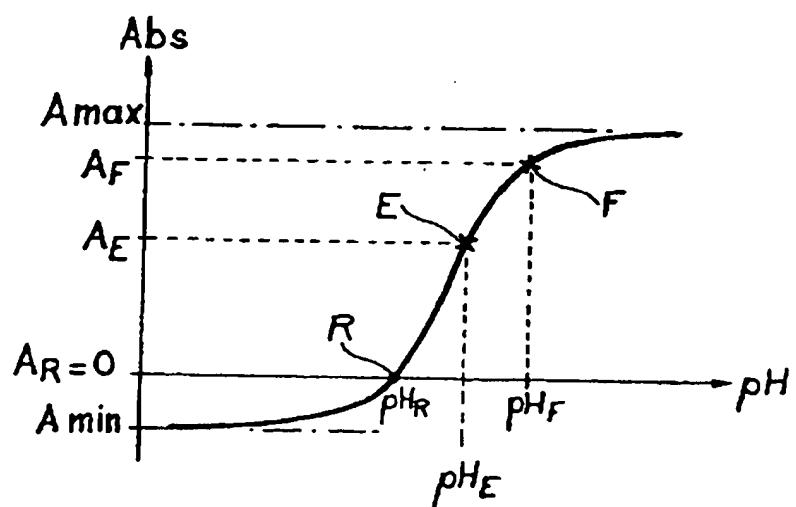


FIG. 6

SEARCH REPORT

Prepared according to the most recent claims
filed before the start of the search

DOCUMENTS CONSIDERED RELEVANT

Category	Document citation, with an indication, as necessary, of the pertinent portions	Affected claims in the examined application
A	JOURNAL OF PHYSICS E/SCIENTIFIC INSTRUMENTS, Vol. 21, No. 1, January 1988, pages 10-17, IOP Publishing, Ltd., Bristol, GB; R. NARAYANASWAMY et al.: "Optical fibre sensors for chemical species" * Figure 5; page 14, column 2, paragraph 3 *	1
A, D	SPIE MICRO-OPTICS, Vol. 1014, 1988, pages 73-76; M. BACCI et al.: "A compact optical fibre device for the detection of pH" * Figure 3; page 74, paragraph 5 – page 75, paragraph 1 *	1
A	EP-A-0 226 822 (HELLIGE GmbH) * Figure 1; page 2, line 20 – page 3, line 7; page 4, line 21 – page 7, line 24 *	1
A	EP-A-0 319 158 (The BOC Group) * Figure 1; column 1, lines 1-3; column 6, line 50 – column 12, line 34 *	1
A, D	SPIE FIBRE OPTIC SENSORS II, Vol. 798, 1987, pages 230-237; K.T.V. GRATTAN et al.: "pH sensor using a LED source in a fibre optic device" * Figure 5; page 234, paragraph 3 – page 235, paragraph 3 *	1

[RIGHT COLUMN]

TECHNICAL FIELDS SEARCHED

(International Class 5)

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Search completed on (date): February 7, 1991

Examiner: U. Zinngrebe

CATEGORIES OF THE CITED DOCUMENTS

- X: Particularly pertinent, in and of itself
- Y: Particularly pertinent, in combination with another document in the same category
- A: Pertinent to at least one claim, or to the overall technological background
- O: Unwritten disclosure
- P: Intercalary [i.e., inserted] document
- T: Theory or principle behind the invention
- E: Patent document bearing a date prior to the filing date, and which was published only on that filing date or on a later date
- D: Cited in the application
- L: Cited for other reasons

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- &: Member of the same family; corresponding document
